Table 2. Intrinsic viscosity measurements on POPG and degraded POPG-TDI polymers

Sample	Concentration c, g/dl	Specific viscosity η_{sp}	η_{sp}/c	Intrinsic viscosity[a] $[\eta]$, dl/g	Average intrinsic viscosity[a] $[\eta]$, dl/g	Intrinsic viscosity[b] $[\eta]$, dl/g	Constant[c] k' calculated
POPG-2000	2.65	0.158	0.0597	0.056	0.0570	0.0576	0.38
	1.93	0.115	0.0597	0.057			
	1.44	0.0852	0.0590	0.057			
	1.16	0.0682	0.0590	0.058			
POPG-3000	2.49	0.235	0.0946	0.087	0.0885	0.0883	0.43
	2.13	0.205	0.0959	0.089			
	1.49	0.140	0.0936	0.089			
	0.996	0.0914	0.0917	0.089			
A	3.14	0.266	0.0850	0.078	0.0785	0.0793	0.31
	2.20	0.185	0.0843	0.079			
	1.46	0.120	0.0821	0.078			
	1.098	0.0897	0.0817	0.079			
B	2.39	0.257	0.1072	0.098	0.1007	0.1027	0.21
	1.40	0.149	0.1064	0.101			
	1.20	0.126	0.1045	0.101			
	0.699	0.0738	0.1056	0.103			
C	1.46	0.105	0.0722	0.069	0.0685	0.0670	0.79
	0.728	0.0506	0.0695	0.068			

[a] These intrinsic viscosities were obtained by calculation assuming $k' = 0.39$ for each concentration.

[b] These intrinsic viscosities were obtained by extrapolation to infinite dilution from the plot of η_{sp}/c versus c.

[c] These values of k' were calculated from the equation $\eta_{sp}/c = [\eta] + k'[\eta]^2 c$ from the plot of η_{sp}/c versus c.

intrinsic viscosities from 0.1 to 0.6 (Ref. 1). In the present work this value has been assumed to be valid for POPG and highly degraded POPG–TDI polymers. Ordinarily η_{sp} is determined for two concentrations and $[\eta]$ calculated from $\eta_{sp}/c = [\eta] + 0.39[\eta]^2 c$. Since the two values of $[\eta]$ generally agree within 0.002 dl/g, use of $k' = 0.39$ is apparently justified. In an effort to determine an experimental value for k' and more adequately assess the possible errors resulting from the assumption that $k' = 0.39$ for POPG and degraded POPG–TDI polymers, some viscosity data at different concentrations have been obtained and are shown in Table 2 and Fig. 3. The solid lines in Fig. 3 have slopes such that $k' = 0.39$; the dashed lines were previously established from the experimental points. Although values of k' from the latter deviate widely from 0.39, the solid lines fit the data within the limits of error and the intrinsic viscosities obtained from either line agree within 0.002 dl/g. Therefore, use of $k' = 0.39$ for polymers of this type should not result in large errors in $[\eta]$. For a unique determination of the true values of k', more accurate data are required. Greater precision could be obtained by increasing the concentration to give higher relative viscosities; however, the results of Fig. 3 indicate that the η_{sp}/c versus c plots may not be linear at concentrations much greater ~2 g/dl.

B. A Study of the Ultimate Properties of Amorphous Gum Vulcanizates

R. F. Fedors and R. F. Landel

1. Introduction

An understanding of the molecular mechanisms which control the ultimate properties of elastomeric materials would be of considerable utility from the standpoint of both theoretical and practical applications. A working theory of the ultimate property behavior of vulcanizates would constitute a long step in contributing a basis for the design of polymeric materials to desired specifications; in addition, once the molecular basis for ultimate property behavior in amorphous gum vulcanizates is understood, then there will be sound basis for understanding the like behavior of filled systems. One pre-

requisite to the formulation or test of any theory is the collection of basic data on the behavior of well characterized vulcanizate systems.

The materials chosen for study are peroxide-cured rubber vulcanizates based on a low temperature styrene–butadiene copolymer generally designated as SBR-1500. The following recipe has been adopted for this study: 1 part Di-Cup R (Dicumyl peroxide) to 100 parts SBR-1500.

This report is concerned primarily with the evaluation and characterization of these specimens by means of "equilibrium" stress–strain, equilibrium swelling behavior, measurement of the sol fraction and measurement of the volume changes on extension.

2. Characterization of Cure

a. Equilibrium stress-strain. From the equation of state for rubber elasticity derived for an ideal rubber, the equilibrium relationship between stress σ_0, concentration of effective network chains per cc of rubber ν_e, and the extension ratio α, is given by (Ref. 3):

$$\sigma_0 = \nu_e RT\left(\alpha - \frac{1}{\alpha^2}\right), \qquad (1)$$

where R is the gas constant in the appropriate units and T is the absolute temperature. Equation (1) is generally found to describe experimental quasi-equilibrium data obtained with real rubbers to a good approximation where $\alpha < 2$. Hence, a plot of σ_0 against the quantity $[\alpha - (1/\alpha^2)]$ should be linear with slope directly proportional to ν_e. The data obtained for the various cures are shown in Fig. 4. The 45-min cure was run in duplicate and the agreement is satisfactory. From the slopes of the curves, the values of ν_e were calculated as a function of cure time and are shown in Fig. 5.

b. Equilibrium swelling. An alternative method of obtaining the concentration of effective network chains per unit volume of rubber is by equilibrium swelling measurements. It has been shown that the relationship between volume fraction of gel in the swollen vulcanizate, v_2 and ν_e for an ideal rubber is given by (Ref. 4, 5, 6):

$$\nu_e = -\frac{(1-s)}{V_0\left[v_2^{1/3}(1-s)^{2/3} - \frac{v_2}{2}\right]} \times \left\{\ln(1-v_2) + v_2 + \sum_{i=1} \chi_i v_2^{i+1}\right\} \qquad (2)$$

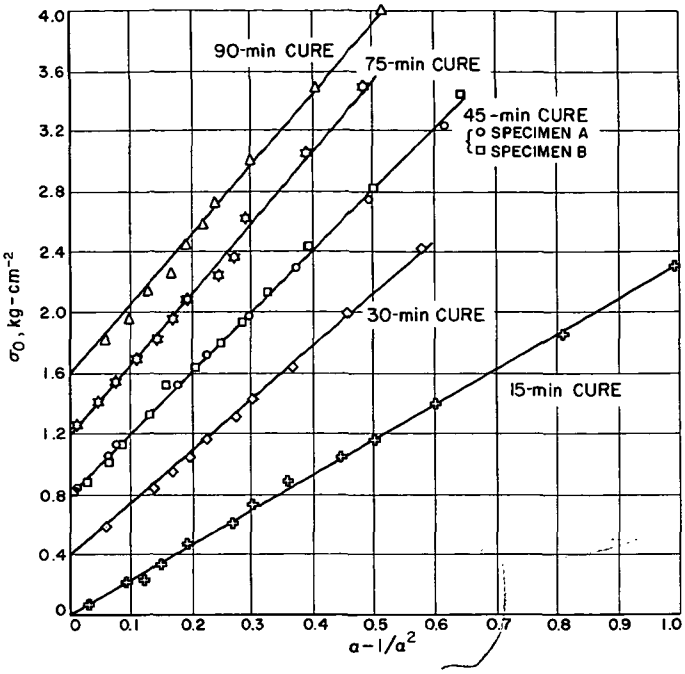

Fig. 4. Stress σ_0, as a function of the form factor $[\alpha - (1/\alpha^2)]$, for different cure times of an SBR-peroxide vulcanizate cured at 150°C

where $\chi_1, \chi_2, \chi_3, \cdots$, essentially represent polymer–solvent interaction coefficients, V_0 is the molal volume of

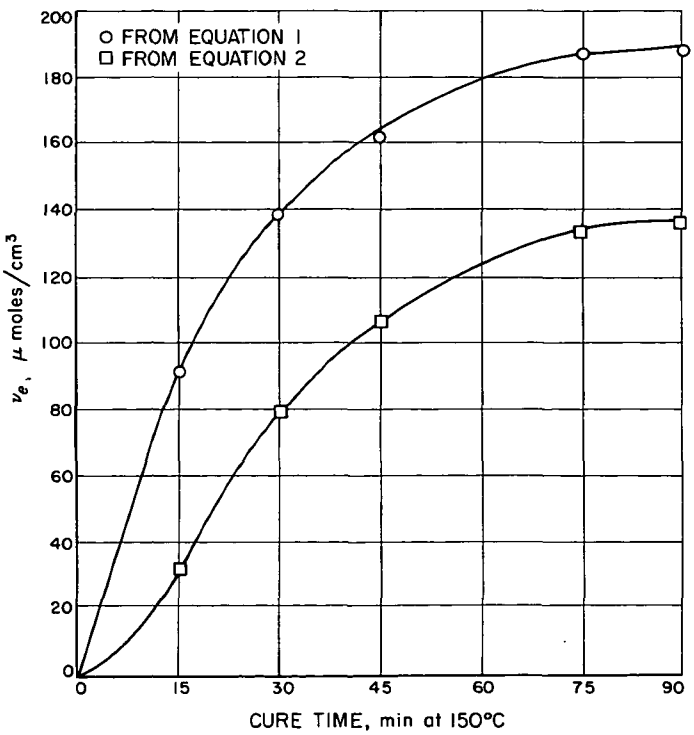

Fig. 5. Dependence of concentration of effective network chains ν_e, on cure time

solvent which for benzene at 23°C is 89.4 $cm^3\ mole^{-1}$, s is the sol fraction and v_2 is the volume fraction of gel rubber in the swollen vulcanizate. The calculated values of ν_e using $\chi_1 = 0.34$ as reported by Smith (Ref. 7) and taking $\chi_2, \chi_3, \cdots = 0$ are shown in Fig. 5.

The divergence between ν_e calculated from the kinetic theory expression, Eq. (1) and ν_e calculated from equilibrium swelling, Eq. (2) is presumably due to two major factors: (1) degradation of the swollen vulcanizates, and (2) the effect on swelling of the nature of the solvent used (Ref. 9). Both sets of data, however, allow an unambiguous selection of the "optimum cure" which for this system turns out to be 75 min. At the optimum cure, changes in the physical properties due to small variations in cure time are at a minimum.

c. Sol-gel ratio. The measured sol fraction as a function of cure time is shown in Fig. 6. In both theory and practice, the partition of polymer molecules between the sol and gel fractions is an important measure of network properties. The sol-gel relationships are particularly simple for the case of the cross-linking of linear primary molecules having a most probable distribution of molecular weights. For this information to be of value, the sol must be a true measure of soluble polymer. It can be shown that the experimental values of s are too large by a factor of about 5. This discrepancy is directly attributable to the extraneous materials such as fatty acids, antioxidants, etc., which are present in the raw polymer before vulcanization.

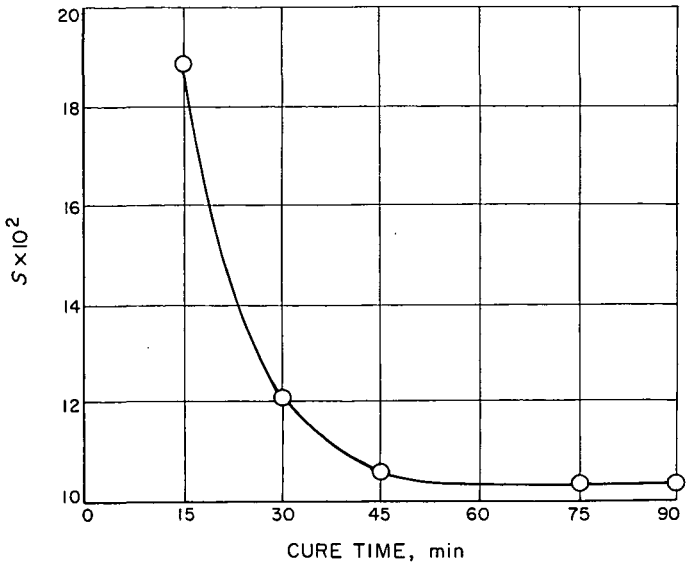

Fig. 6. Fraction of soluble material as a function of cure time

3. Physical Properties

a. Volume changes on extension. For the intended study of ultimate property behavior it is important to have knowledge of the change in volume on extension, especially for extensions approaching the ultimate. The method of hydrostatic weighing was used as a measure of volume changes. A rig was made up whereby four tensile ring specimens could be stretched under water in 0.5-in. increments. The totally immersed rig and either relaxed or extended specimens were suspended by a 10-mil platinum wire from a Mettler balance which was mounted on an essentially vibration-proof table. The results are shown in Fig. 7, where the weight of the immersed rig and specimens is shown as a function of time of immersion and extension ratio of the specimens. The filled circles represent the weight of relaxed specimens; the other symbols denote the weight at the various extension ratios. The change in weight on extension was taken as the difference in weight of the extended specimens and the weight of the relaxed specimens as interpolated from the linear portion of the curve.

Relative volume changes with extension are shown in Fig. 8. Data are also shown for SBR-peroxide vulcanizates (Ref. 11) and for natural rubber peroxide vulcanizate (Ref. 10) taken from the literature. Few data are available for comparison at large extension ratios, but Kusov et al. (Ref. 12) have also reported that the relationship between relative volume and strain yields an S-shaped curve.

The specimens ruptured at $\varepsilon = 3.1$, and even at break, the change in volume is only of the order of 0.06%. From the data of Fig. 8, values of the logarithmic Poisson ratio at various strains were calculated from (Ref. 8):

$$\frac{d(\ln V/V_0)}{d(\ln\lambda_1)} = 1 - 2\nu \qquad (3)$$

where V is the volume at any extension ratio λ_1, V_0 is the volume of the unstrained material and ν is Poisson's ratio. The results are shown in Fig. 9. It is to be expected that volume changes on extension will become more and more significant as the temperature decreases, i.e., as T_g is approached. Poisson's ratio should decrease from 0.5 to about 0.3 (Ref. 13). Therefore, volume changes on extension will be measured at selected low temperatures.

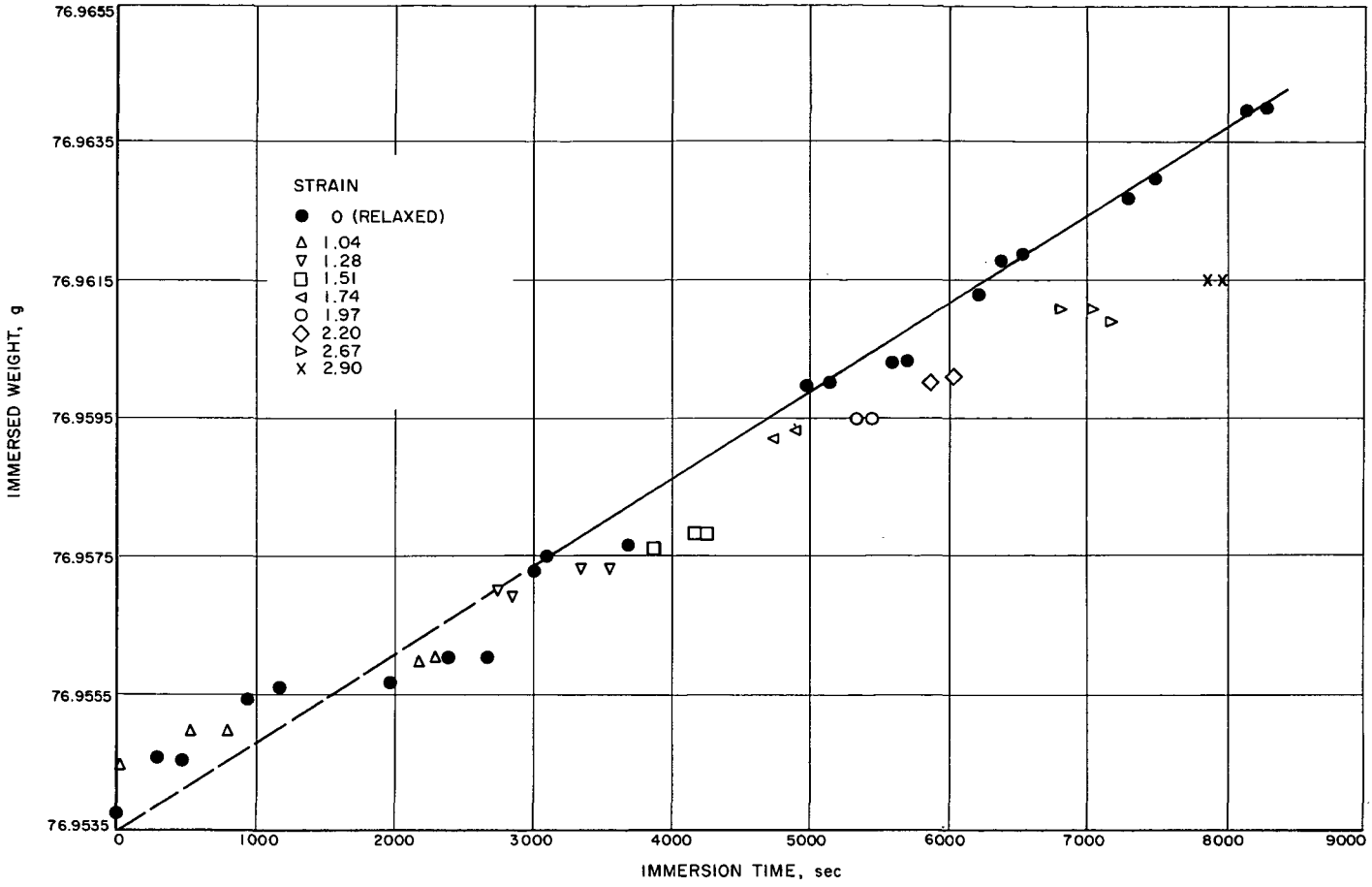

Fig. 7. Dependence of immersed weight on immersion time and strain

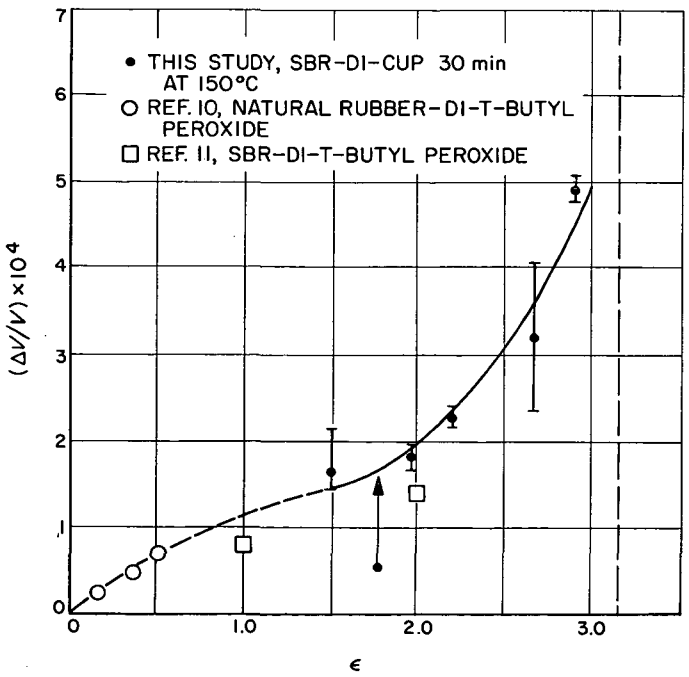

Fig. 8. Change in relative volume as a function of strain

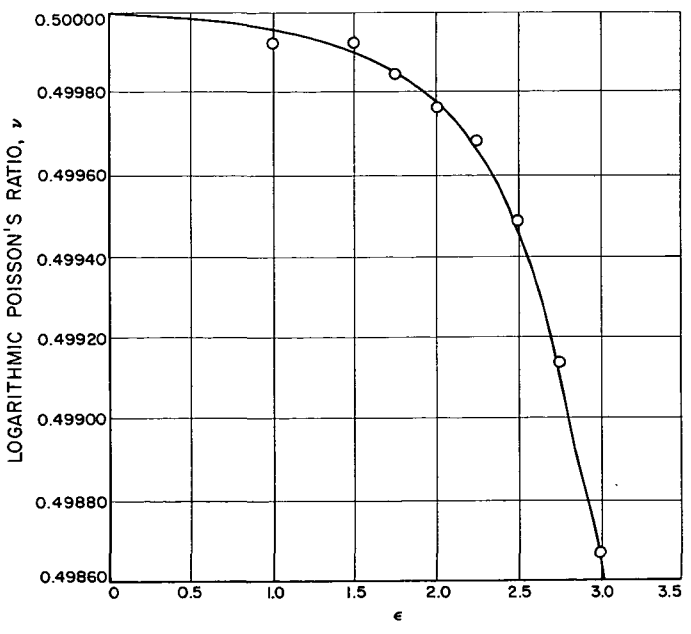

Fig. 9. Logarithmic Poisson's ratio ν, as a function of the strain ε